

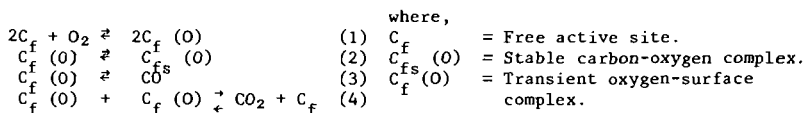
VARIATIONS IN THE OXYGEN CHEMISORPTION CAPACITY
OF MILD GASIFICATION CHAR AT VARIOUS LEVELS OF BURNOFF

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INTRODUCTION AND BACKGROUND

Our results demonstrated that by careful selection of coal devolatilization conditions, it is possible to produce high quality (but, perhaps, low yield) liquid fuels (1). However, the overall economics of a devolatilization process is strongly influenced by the commercial use of char which constitutes as the major portion of the devolatilization products, regardless of pyrolysis scheme utilized. Coal chars prepared by low-temperature devolatilization have a higher degree of crystallinity than the starting coal. However, the crystalline structure of coal char is significantly less ordered than graphite. The lower the coal pyrolysis temperature, the greater the disorder. In graphite, the building blocks are lamellar in structure held together by van der Waals forces. At the edge, crystallites have unpaired sigma electrons which are susceptible to attack by oxidants. The edge carbon atoms are more reactive than basal carbon atoms. Active carbon sites are considered as dislocations or imperfections in the crystallite edges of carbon (2). It was demonstrated (1) that chars prepared at mild conditions (i.e., 500°C) had higher active surface areas, and thus had higher reactivity than those prepared at severe conditions (i.e., 950°C). Numerous studies have been reported on the reactivity of chars generated at different operating conditions, (e.g., different char formation temperatures, burnoff temperatures, oxygen partial pressures, and particle sizes) (1-4). The factors which influence the reactivity of coal char include the following: (a) concentration of carbon active sites, (b) catalysis by the inherently present minerals, and (c) the diffusion of the reactant and product gases within the pores of the devolatilized char (3). Coal chars are heterogeneous materials that can contain significant amounts of heteroatoms such as hydrogen, oxygen, nitrogen, and sulfur, which may also influence the reactivity. While oxygen sites influence reactivity by electron exchange, nitrogen and sulfur sites encourage ring attack due to concentration of the electrons (2). It was demonstrated that the char's hydrogen content can play a significant role in reactivity perhaps by providing a source of nascent-carbon sites (1).

Numerous studies considered the significance of active surface area for investigating the reactivity of coal char or carbon (9-14). The technique used to determine the concentration of carbon active sites is oxygen chemisorption. Laine et al. (4) investigated the role of the active surface area in the carbon-oxygen reaction, and observed that the unoccupied (i.e., available) active surface area was the major factor that determines the rate constant, rather than the conventional Brunauer-Emmett-Teller (B.E.T.) surface area. Although carbon-oxygen reactions have widely been investigated (2-18) and several mechanisms postulated, the exact mechanisms are not well understood. Several elementary reactions (shown below) have been used (2) to describe the reaction mechanisms:



On the basis of active surface area, the rate constants of carbon-oxygen reactions were calculated using an equation of the form:

$$\frac{dP_{O_2}}{dt} = k (P_{O_2}) (UASA) \quad \text{where, } UASA = ASA(1-\theta) \quad (5)$$

ASA is the active surface area for the char, and $(1-\theta)$ is the fraction of the ASA which is unoccupied (UASA). Laine et al (4) calculated rate constants based on both UASA as well as total surface area (TSA), determined by BET measurements. On the basis of UASA, the calculated rate constants were essentially constant over the burnoff and time range studied. According to this theory, available active surface, as determined by oxygen chemisorption capacity is a fundamental property of a coal char which influences its reactivity.

From a gasification or combustion standpoint, the sites participating in gasification can be significantly different from those measured initially, i.e., before any burnoff occurs. Chornet et al. (15) assumed that the char-oxygen reaction system undergoes three sequential phases: (a) initially, the reaction proceeds slowly because the inventory of "active sites" is rather limited at the onset of the reaction; (b) acceleration of the reaction rate occurs because the concentration of active sites increases significantly due to pore growth and opening, and a maximum rate reflects a balance between generation and depletion of these active sites; and (c) beyond this maximum point, the total number of active sites and thus, the reaction rate, decrease due to the consumption of active sites during burnoff. However, no experimental work was performed to validate this model. Mahajan et al. (16) suggested that the availability of active sites might be controlled by the opening and loss of the pores during oxidation in a complex way.

The normalized burnoff rate has been extensively used in the literature for studying coal char combustion. Arbitrarily defined reference times such as 10-, 15-, or 50-percent conversion for maximum reactivity have been used by various investigators (1,9,18,21). For example, while Mahajan et al. (16) normalized reactivity results based on the time needed for 50 percent burnoff, Solomon et al. (17) developed a new approach for normalizing the reaction rate based on 10 percent burnoff, implying that various reference times used may have fundamental significance. The significance of various reference times on normalization of char reactivity is not well understood. The objectives of this study are: (a) to investigate the variation in ASA as a function of burnoff, and (b) to study the influence of various reference times (from 10- to 70-percent burnoff) on a normalized reaction rate.

EXPERIMENTAL

As described elsewhere (1), a Pittsburgh No. 8 (high-volatile bituminous) coal was pyrolyzed in a thermogravimetric analysis (TGA) system heated at 20°C/min in an inert atmosphere. Low-temperature char was prepared at 500°C while the high-temperature char was prepared at 950°C. Operating conditions for oxidation as well as the technique that was used to monitor the isothermal burnoff rate have been described in detail (1). Selected chars were then subjected to oxidation in a TGA system at burnoff temperatures of 400 to 474°C. Char weight loss was monitored continuously during the reaction period and was converted to the fractional char burnoff at various times (Figure 1). The reactive gas had a flowrate of 120 mL/min oxygen. The oxygen chemisorption capacity (OCC) was determined by measuring the oxygen uptake by the coal char at approximately 200°C and 0.1 MPa of oxygen for about 15 hours in a TGA system. The oxygen chemisorption capacity for the low- and high-temperature chars are 203 and 70 m²/g, respectively. Obviously, the results demonstrate that the low-temperature chars have a significantly higher OCC than the high-temperature chars. These and other related results have been discussed elsewhere (10) in detail.

RESULTS AND DISCUSSION

Normalization of Burnoff Curves Using Various Reference Times

The instantaneous weight of char in a typical TGA run is monitored continuously during the reaction period. The fractional char conversion (f) is generally used to represent the characteristic of char burnoff. The values of f at any time during char burnoff can be calculated from the TGA weight-loss curve using the following expression:

$$f = \frac{M(0) - M(t)}{M(0) - M_{\text{ash}}}$$

where M_0 is the initial weight of char, M_t is the instantaneous weight of char, and M_{ash} is the ash content in the original char sample. The time scale can also be normalized to the dimensionless time τ , based on the reference time $t_{0.5}$. Figure 1 compares the fractional burnoff curves for chars prepared at 500° and 950°C. For the 500°C char, there is a maximum burnoff rate at about 10 percent of char burnoff. The shape of the combustion curve (i.e., changing slopes) possibly reflects the competing events of pore growth and pore depletion as proposed by others (3,16). Lizzio et al. (19), suggested that this observed maximum rate is not caused by decreasing intraparticle diffusional limitations, but rather is a result of competing mechanisms as described by other investigators (15,16) in the kinetically controlled regime.

Upon normalization of the burnoff rate, there is only one characteristic burnoff curve for any burnoff temperature. For example, Figure 2 (a,b) shows some of the burnoff curves for the 500°C char oxidized at burnoff temperatures of 400 to 474°C. These burnoff curves have been normalized with the time required for 10- to 70-percent char burnoff corresponding to each T_b . The curves are very similar to each other and can be considered as a single characteristic curve. Also, similar results were obtained for the 950°C char oxidized at $T_b = 400, 430, \text{ and } 450$ as shown in Figure 2 (c,d).

The data for 50 percent burnoff cases is not shown. The unique characteristic burnoff curve for each char preparation temperature facilitates analysis of data at different temperatures. However, these data demonstrate that there is little fundamental significance of the burnoff time used for normalized reactivity data.

Oxygen Chemisorption Capacity (OCC) of a Low-Temperature Char Measured at Various Levels of Burnoff

The variation of OCC with fractional burnoff was monitored in a TGA system for the 500°C char. The char was heated to 400°C in helium before pure oxygen was introduced into the reactor at the same temperature. At each level of burnoff, the burned char was subjected to measurement of OCC by oxygen chemisorption at 200°C. The level of burnoff measured in this study ranged from zero to 85 percent (dry-ash-free char basis). Results of the OCC measurement at different burnoff levels are shown in Figure 3. Several interesting observations can be made about this data. First of all, the measured OCC in this study are very high compared to those generally reported in the literature for coal chars. The ASA was calculated assuming that chemisorption is dissociative and each oxygen atom occupies one carbon atom with a cross sectional area of 83 \AA^2 . Such assumption, though reasonable for pure graphite, may not be strictly valid for highly amorphous char where oxygen may sorb on surface without dissociation. This high-surface area perhaps reflects that the low-temperature chars (500°C) are indeed highly amorphous and, therefore, have the highest concentration of reactive sites. Second, the measured peak in OCC does not necessarily coincide with the peak in reactivity. In fact, the maximum reactivity as a function of burnoff occurs at 10 percent burnoff where the OCC is much lower. The maximum OCC occurs at about 60 percent burnoff. Therefore, the changes in OCC does not correlate with the reactivity as a function of burnoff. Several other researchers also faced difficulties in correlating rate constant with active surface area. Using the same procedure as Laine et al. (4), Taylor and Walker (23) measured ASA for partially oxidized samples of Saran char. Their attempts to measure UASA led to the conclusion that there was no correlation between ASA and reactivity.

An alternative approach to the ones taken by Laine et al. (4) can be considered (18). One can argue that in addition to gaseous products generated by the "transient" carbon-oxygen surface intermediates, the decomposition of the "stable" carbon-oxygen complex also contributes to gasification. The reaction rate of the samples with oxygen can be described by:

$$-\frac{dP_{O_2}}{dt} = k_e (P_{O_2}) (UASA) + k_b (P_{O_2}) (TSA) \quad (7)$$

Where k_e and k_b represent the reaction rate constants for attack at the edge and basal plane carbon atoms, respectively. If $k_e \gg k_b$, upon some activation by carbon to produce a large amount of ASA, the first term of the above equation dominates.

Su and Perlmutter (18) considered that the rate constants for char oxidation cannot be described based solely on UASA. According to these authors, all surface (stable or transient oxygen-complex) sites are important for coal char. Coal chars are more disordered than the graphon studied by Laine

(whose surface is composed mainly of unreactive basal planes with very few edge sites). While Laine et al. (4) proposed that deposited oxygen tend to retard reaction, we note in this study that the reactivity was highest when OCC (unoccupied active surface area) was very low. This suggests that the stable complexes may play an important role for char oxidation, especially the chars that are highly amorphous. Keeping this in mind, Su and Perlmutter (18) proposed the following elementary reactions:



k_a = rate constant for oxygen adsorption on carbon.
 k_a^- = rate constant for reversible desorption.
 k_a^+ = rate constant for oxygen decomposition on char.
 k_d = rate constant for direct burnoff.

The mechanism proposed by Su and Perlmutter (18) emphasizes the importance of stable sites in determining the reactivity of carbon-oxygen reaction. The present study suggests that the mechanism developed by Laine, et al., is not directly applicable for the low-temperature char used in this investigation.

The results shown in Figure 3 suggest that there may be three competing phenomena related to the change of OCC during char burnoff. During the early stage of char burnoff, the only active sites available for chemisorption are those that present on the char surface. These char active sites form stable C-O complexes by chemisorption, but not all sites undergo decomposition at the reaction temperature of 400°C. Thus, the inventory of unoccupied active sites, is greatly reduced during the initial stages of char oxidation by the formation of stable carbon-oxygen complexes. Our unpublished results showed that as oxygen was introduced at 400°C, the sample showed a significantly rapid weight gain. Nonisothermal heating in air of coal chars, which were prepared from coals of various ranks, also showed the significant increase in sample weight at various temperature ranges, depending on the coal rank. These results suggest the formation of stable C-O surface complexes that would occupy a significant amount of active sites. Guerin et al. (22), Floess et al. (20), and Lizzio et al. (19) have recently made similar observations. As the char continues to burn, a competing process, the opening of fresh sites previously closed that reside on micropore walls, plays the dominant role in increasing the amount of active sites. For a char burnoff between 35 and 65 percent, micropores in the inner core of the char may open up to expose more chemisorption sites to the bulk gas phase. At 55-percent burnoff, the active surface area reaches its maximum, indicating that the accessibility of unoccupied active surface area caused by opening of previously closed pore also reaches its maximum. As the walls between existing pores are burned away, the total number of open pores, as well as active sites, start to decrease. Beyond 65-percent burnoff, the

total availability of active sites decreases. At still higher burnoff (e.g., 85-percent burnoff) the amount of OCC is reduced to its initial amount of about 200 m²/g.

In summary, the measured oxygen chemisorption capacity can be explained by three competing mechanisms. This study provides credence to the hypothesis proposed by Chornet et al (15) (at least the second and third stages of the proposed reaction schemes seem to follow the events observed in this study). The competing events proposed in this study, however, require additional validation perhaps by measurements of the total surface area of the char at various levels of burnoff. Furthermore, significance of measured oxygen chemisorption capacity and the role of stable and unstable oxygen-carbon complexes on the reactivity of char at various burnoff levels warrants further investigation.

SUMMARY AND CONCLUSIONS

The results of this study demonstrate that the conventionally defined unoccupied active surface area, as determined by oxygen chemisorption capacity at various levels of burnoff, does not seem to strictly correlate with the reactivity rate at various levels of burnoffs. This study suggests that stable sites may play a key role in reactivity, but their exact role at this stage of investigating is only speculative. The observed phenomenological changes in the measured OCC (active surface area not occupied by stable sites), as determined by oxygen chemisorption, at various levels of burnoff have been explained in terms of three competing mechanisms: (a) depletion of active sites available on the char surface caused by formation of a stable C-O complex, (b) increase of nascent active sites because of pore opening, and (c) decrease of OCC in the final stage of burnoff because of pore wall burnoff. The normalized reaction rate, based on a 10- to 70-percent burnoff time for different reaction temperatures, resulted in a single characteristic curve for a given type of char that was reacted at any reaction temperature. This finding suggests that the different reference times used widely in the literature do not necessarily signify parameters of fundamental importance.

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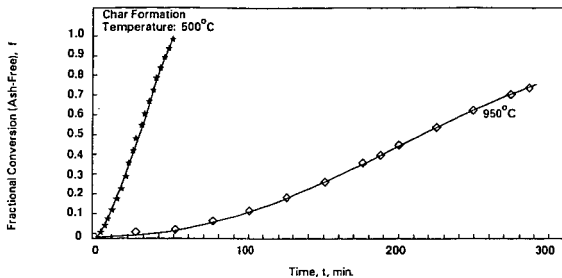


Figure 1. Fractional Burnoff Curves for Chars Prepared from Pittsburgh No. 8 Coal at 500°C and 950°C; Burnoff Temperature 400°C

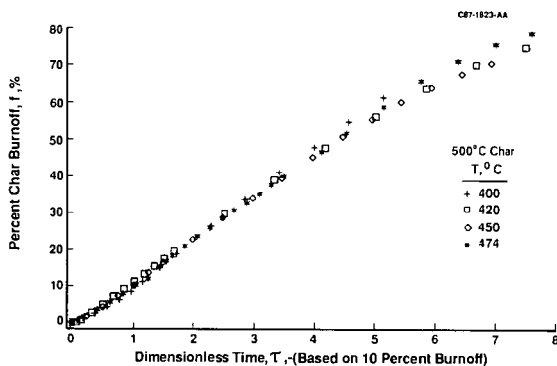


Figure 2a. Normalized Burnoff Curves for 500°C Char Oxidized at 400°, 420°, 450°, and 474°C

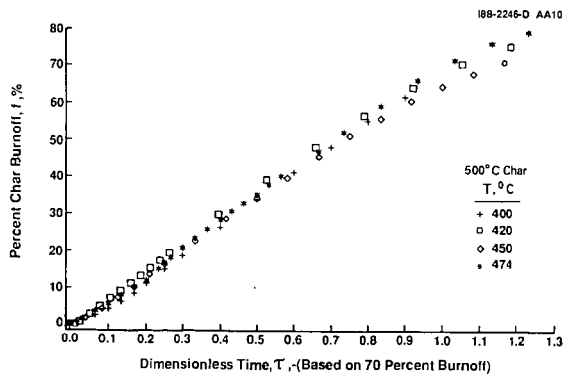


Figure 2b. Normalized Burnoff Curves for 500°C Char Oxidized at 400°, 420°, 450°, and 474°C

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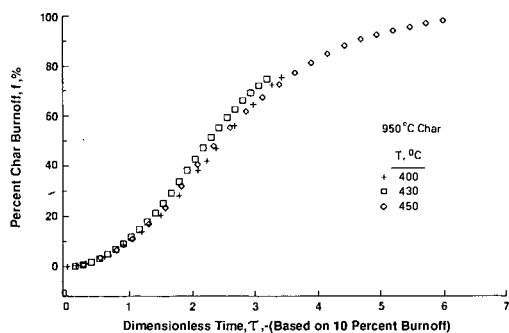


Figure 2c. Normalized Burnoff Curves for 950°C Char Oxidized at 400°, 430°, and 450°C

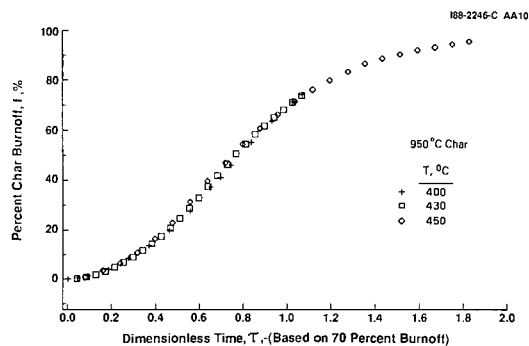


Figure 2d. Normalized Burnoff Curves for 950°C Char Oxidized at 400°, 430°, and 450°C

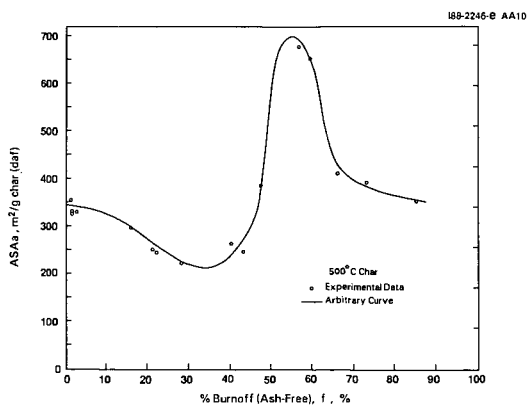


Figure 3. Changes in the Measured Active Surface Area (ASA) as Determined by Oxygen Chemisorption at Different Burnoff Levels of 500° C Char (Oxidized at 400° C)